

Reactivity of CF_n ($n=1-3$) radicals with a silica surface

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Abstract

The trends in reactivity of CF_n radicals with SiO_2 and the site selectivity of the attack are studied using two different cluster models. The reaction barriers for the most energetically favorable reaction are computed. It is shown that CF_n radicals are fairly unreactive towards SiO_2 .

keywords: clusters; Density functional theory; Surface chemical reaction; Silicon oxides

I. INTRODUCTION

Etching of SiO_2 using fluorocarbon plasmas involves several neutral as well as charged species. Radicals such as CF_3 , CF_2 , and CF are expected to play an important role. Several experimental studies have been performed to determine the reactivity of CF_2 and CF_3 . An early experiment by Brannon [1] showed that, in the presence of an intense photon field, CF_2 radicals, from photolyzed CF_2Br_2 , are capable of etching silicon dioxide. However a more recent study by Langan *et al.* [2] determined that laser-generated CF_2 adsorbs on silicon dioxide surfaces, but does not dissociate or etch the SiO_2 surface. They also showed that ion bombardment leads to a loss of adsorbed CF_2 instead of a fluorine transfer reaction at the surface. Butterbaugh *et al.* [3]

simulated the major species present in fluorocarbon plasmas using F and CF₂ beams and a beam of Ar⁺. They concluded that energetic Ar⁺ bombardment enhances the etching yield of SiO₂ for both CF₂ and F. However, when CF₂ and F beams are used simultaneously, F dominates and CF₂ has little effect. Robertson *et al.* [4] investigated the reactions of CF₃, generated from CF₃I by IR-multiphoton decomposition, with SiO₂ surfaces. Their results showed that no spontaneous etching occurs. Similar conclusions were obtained by Joyce *et al.* [5] who also showed that sputtering the oxide surface by argon ion bombardment increases the amount of radicals that can be adsorbed. Overall the reactivity of CF₃ appears to be below experimental detection limits [3] and adsorbed CF₃ appears to be mainly bound to O atoms of SiO₂ [6].

A theoretical study of the reactivity of CF_n ($n=1-4$) radicals with SiO₂ has been performed by Jenichen [7] using ab initio methods and cluster models. The work assumes that CF_n species form O-C bonds and focuses on the breaking of a Si-O bond with simultaneous transfer of a F atom to a Si atom via a cyclic transition state.

At the present time the trends in reactivity of CF_n radicals with SiO₂ are not fully understood and the preferred sites of attack need to be confirmed based on relative energies. Reaction barriers are also of interest.

In the present work we use Density functional theory (DFT), in conjunction with the cluster model approach, to investigate the energetics of several reactions of CF_n ($n=1-3$) radicals with SiO₂ models and the reaction barriers for some key reactions.

II. METHODS

At the surface, the SiO₂ structure terminates in either a siloxane group (SiOSi) or a silanol group (SiOH). We model the silanol surface group using Si(OH)₄ (see Fig. 1a) and the siloxane group using (HO)₃SiOSi(OH)₃ (see Fig. 1b).

All the geometries are fully optimized using the hybrid [8] B3LYP [9] approach,

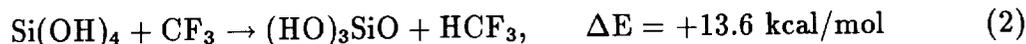
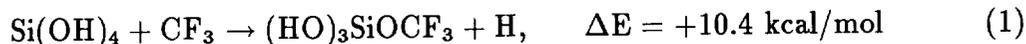
in conjunction with the 6-311++G** basis set [10]. The harmonic frequencies are computed to determine if the structures are at local minima or saddle points and to obtain the zero-point energies. The search for the transition state (TS) geometries is aided by computing the force constants at every point to ensure the correct curvature. The energetics of the reactions are computed at the B3LYP/6-311++G** level of theory. All of the B3LYP calculations are performed using Gaussian94 [11].

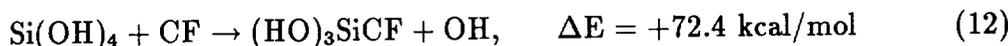
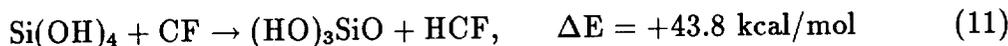
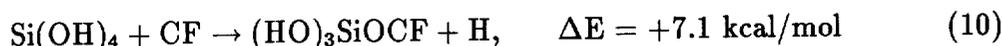
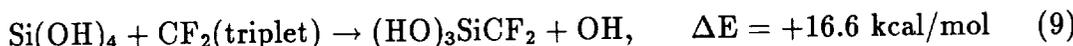
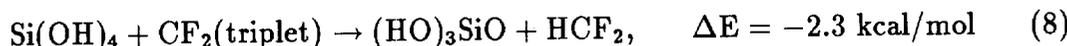
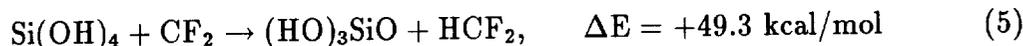
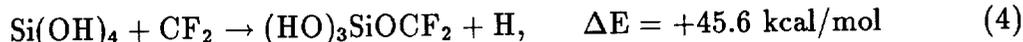
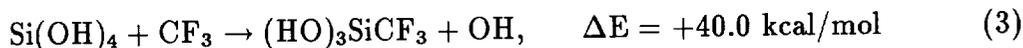
III. RESULTS AND DISCUSSION

We first consider the reactions of the CF_n ($n=1-3$) radicals with the simplest model, $Si(OH)_4$. This model, which is too simple to represent the real SiO_2 surface, is nevertheless sufficient to provide relative energies and trends in reactivity. Three of the OH groups are considered to be part of the surface and the fourth OH is used to model the surface OH.

For CF_3 the ground state (GS) is a doublet state (2A_1) with C_{3v} symmetry while for CF_2 the ground state is a singlet state (1A_1) with C_{2v} symmetry. The lowest CF_2 triplet state (3B_1) lies 51.7 kcal/mol (2.24 eV) above the 1A_1 state. For CF the ground state is a doublet state $^2\Pi$ and the nearest quartet state ($^4\Sigma^-$) is 83.9 kcal/mol (3.64 eV) higher in energy. Because of the high energy separation between the doublet and quartet states for CF we only study the reactions of CF $^2\Pi$ whereas for CF_2 we study both the reactions of the 1A_1 and 3B_1 states.

We consider three possible sites of attack on $Si(OH)_4$ by the carbon atom of CF_n : 1) the O atom of the surface OH, 2) the H atom of the surface OH, and 3) the Si atom. The reactions studied and their corresponding energetics are reported in Eqns 1-12. The CF_n species are in their ground state unless reported otherwise.

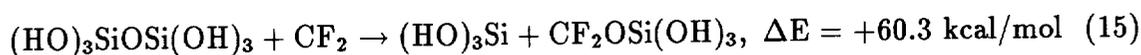
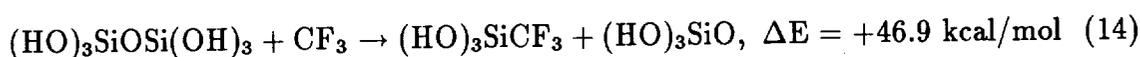
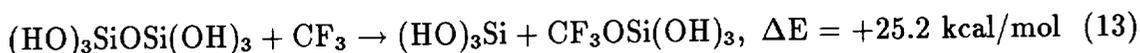




A comparison of the various energies shows that for all CF_n species the most energetically favorable reaction corresponds to the attack of the O atom with concomitant breakage of the O-H bond. On the other hand the attack of the Si atom is the least favorable energetically. These results are in agreement with the experiments of McFeely *et al.* [6]. All the reactions for the CF_n species in their ground states are endothermic and therefore are only important at high temperatures or if energy is added by ion bombardment. CF_3 and CF have very similar reaction energies with respect to the attack of the O atom and their reactions are the most favorable energetically. However, for the attack of the H atom, CF_3 and CF behave differently, with CF_3 being considerably less acidic than both CF and CF_2 . CF_2 in its ground state is very unreactive due to the fact that in its singlet state it cannot form a bond without promotion from the singlet state to the triplet, which requires 51.7 kcal/mol (2.24 eV).

As a second step we consider the reactions of the CF_n ($n=1-3$) radicals with the $(\text{HO})_3\text{SiOSi(OH)}_3$ model. Two possible sites of attack by the C atom of CF_n are

considered: 1) the O atom of the siloxane (Si-O-Si) group and 2) the Si atom. The reactions investigated and their corresponding energetics are reported in Eqns 13-16. The CF_n species are in their ground state unless reported otherwise.



The results show that the attack of the O atom in the Si-O-Si group with concomitant breaking of the Si-O bond is less favorable energetically than the attack of the O atom in the surface OH group of $Si(OH)_4$ with concomitant breaking of the O-H bond due to a greater bond strength of Si-O compared with O-H. The attack of the Si atom in the SiOSi group by CF_3 is slightly less favorable than the attack of the Si atom in the SiOH group but still comparable in energy. This result confirms that the attack of the Si atom is energetically unfavorable.

The energy barriers for the reaction of $Si(OH)_4$ with CF_n ($n=1-3$) are reported in Table I. The energy barrier varies as a function of the fluorocarbon group as follows:



The high energy barrier for CF_2 is not surprising as the reactions of $Si(OH)_4$ with CF_2 in its ground state are very endothermic (see Eqns (4)-(6)). It is however interesting to note that CF_2 in its triplet state also has a large barrier. We can therefore conclude that CF_2 is unreactive towards SiO_2 . CF has the lowest energy barrier and it is more reactive than CF_3 . However the energy barrier for CF is still fairly high and it is unlikely that CF would react with SiO_2 at moderate temperatures.

The transition state geometries for the reactions reported in Eqn. (1), (4) and (10) are shown in Figs 2-4. For CF (see Fig. 2) and CF_2 (see Fig. 3) the TS has a

product-like structure in agreement with the fact that the energy barrier going from the products to the TS (ΔE_P) is the smallest for CF and CF₂. For CF₃ (see Fig. 4) the TS structure is the average between the structure of the reactants and of the products in agreement with similar values for ΔE_R and ΔE_P .

We can conclude from both the reaction energetics and the barriers that CF_n radicals are quite unreactive towards SiO₂ in agreement with experimental results which showed that no spontaneous etching of SiO₂ occurs using only fluorocarbon plasmas. The lack of dangling bonds on the SiO₂ surface inhibits reactions with radicals. Ion bombardment can produce dangling bonds at the surface by breaking Si-O bonds and therefore increases the reactivity of CF_n radicals with the SiO₂ surface. Ion bombardment can also provide the necessary energy to drive the endothermic reactions.

IV. CONCLUSIONS

CF_n radicals are fairly unreactive towards SiO₂. All the reactions for CF_n systems in their ground states are endothermic. The most energetically favorable reaction corresponds to the attack of the O atom in the surface OH group of Si(OH)₄ by the C atom of CF_n. The reactivity of the CF_n radicals in their ground states follows the order: CF > CF₃ > CF₂. CF₂ is very unreactive due to the fact that its singlet state cannot readily form a bond without promotion to a higher triplet state. CF has the lowest energy barrier and it is more reactive than CF₃.

V. ACKNOWLEDGMENTS

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TABLES

TABLE I. Energy barrier (kcal/mol) for the reaction of Si(OH)_4 with CF_n ($n=1-3$) leading to $(\text{HO})_3\text{SiOCF}_n + \text{H}$ computed using B3LYP/6-311++G** and with zero-point energy correction. The CF_n species are in their ground state unless reported otherwise.

Fluorocarbon	ΔE_R^a	ΔE_P^b
CF_3	46.5	36.1
CF_2	58.0	12.4
CF_2 (triplet)	32.9	38.9
CF	22.4	15.3

^a ΔE_R means that the energy barrier is from the reactants to the transition state.

^b ΔE_P means that the energy barrier is from the products to the transition state.

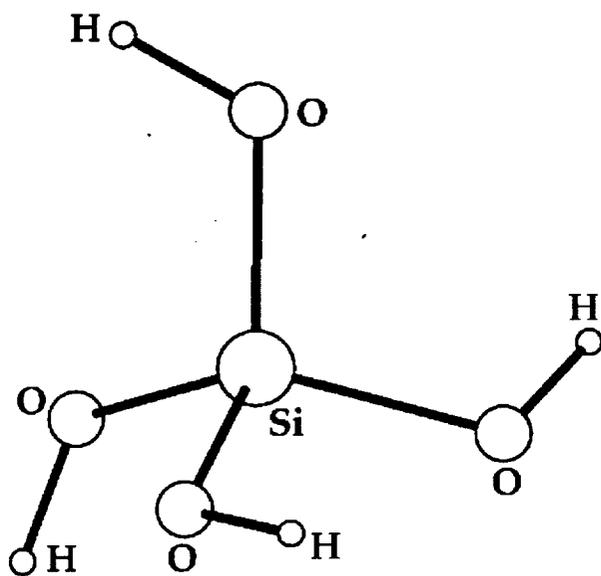
FIGURES

FIG. 1. Geometric structure of the SiO_2 models: (a) $\text{Si}(\text{OH})_4$; (b) $(\text{HO})_3\text{SiOSi}(\text{OH})_3$.

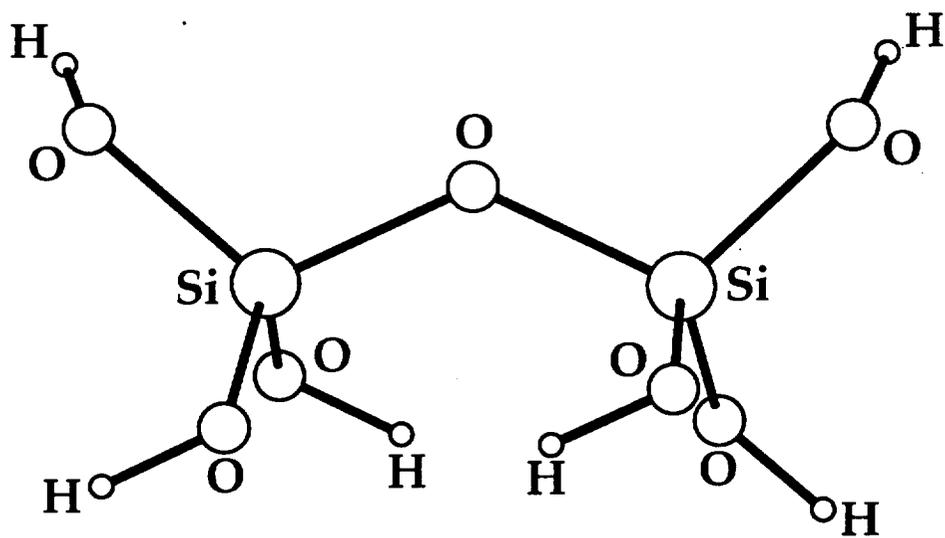
FIG. 2. Transition state geometry for the reaction of $\text{Si}(\text{OH})_4$ with CF (in its ground state) leading to $(\text{HO})_3\text{SiOCF} + \text{H}$. The bond lengths are in angstroms.

FIG. 3. Transition state geometry for the reaction of $\text{Si}(\text{OH})_4$ with CF_2 (in its ground state) leading to $(\text{HO})_3\text{SiOCF}_2 + \text{H}$. The bond lengths are in angstroms and the bond angles in degrees.

FIG. 4. Transition state geometry for the reaction of $\text{Si}(\text{OH})_4$ with CF_3 (in its ground state) leading to $(\text{HO})_3\text{SiOCF}_3 + \text{H}$. The bond lengths are in angstroms and the bond angles in degrees.



a



b

Fig. 1

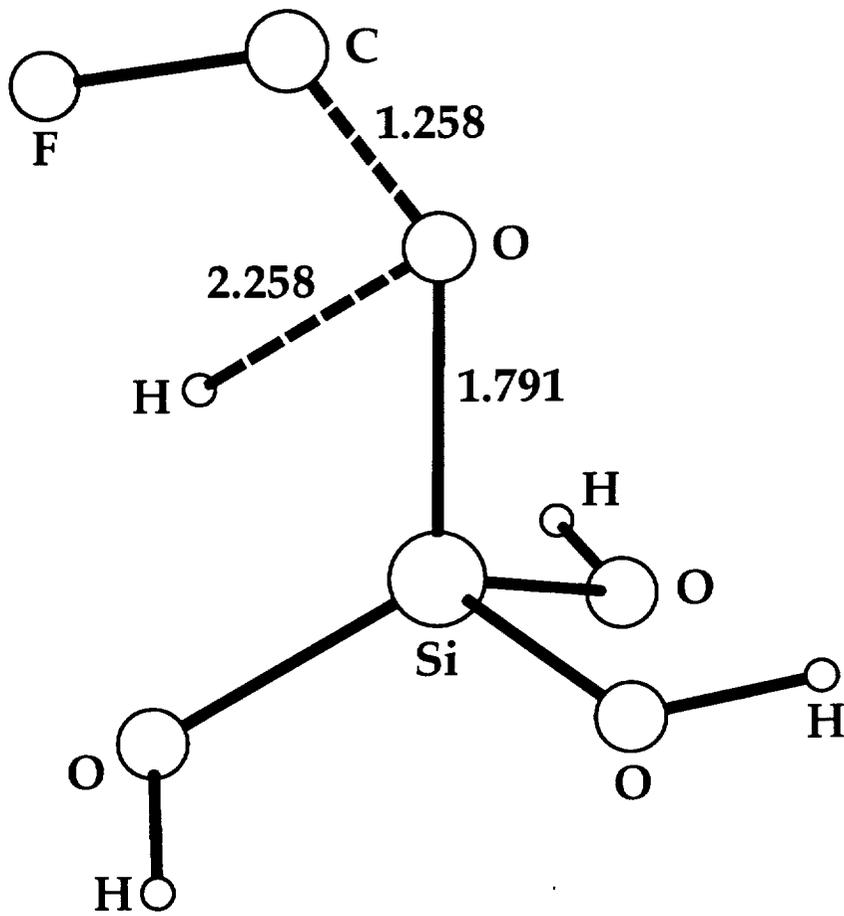


Fig 2

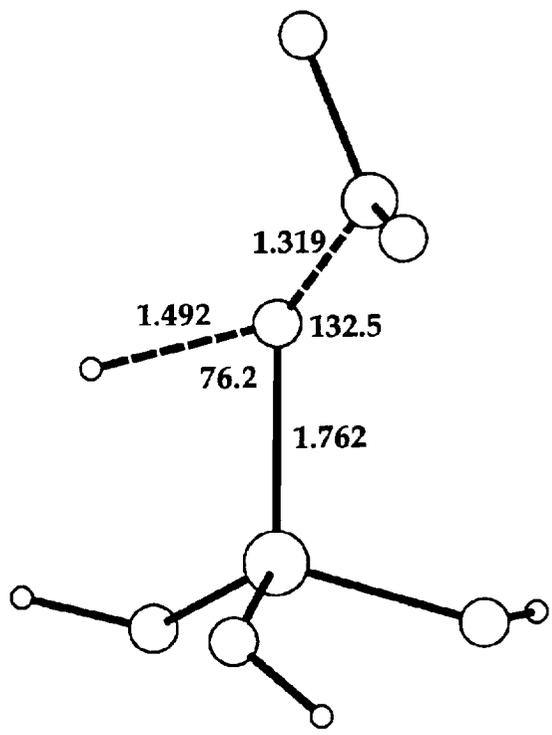
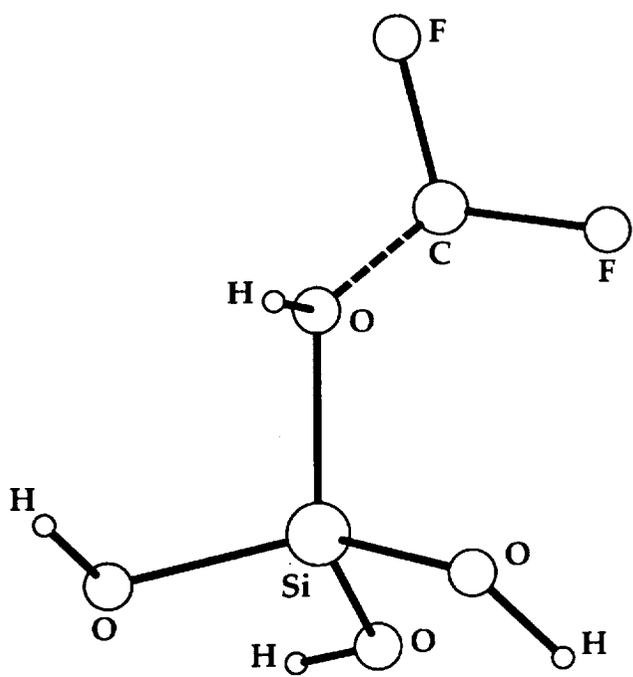


Fig 3

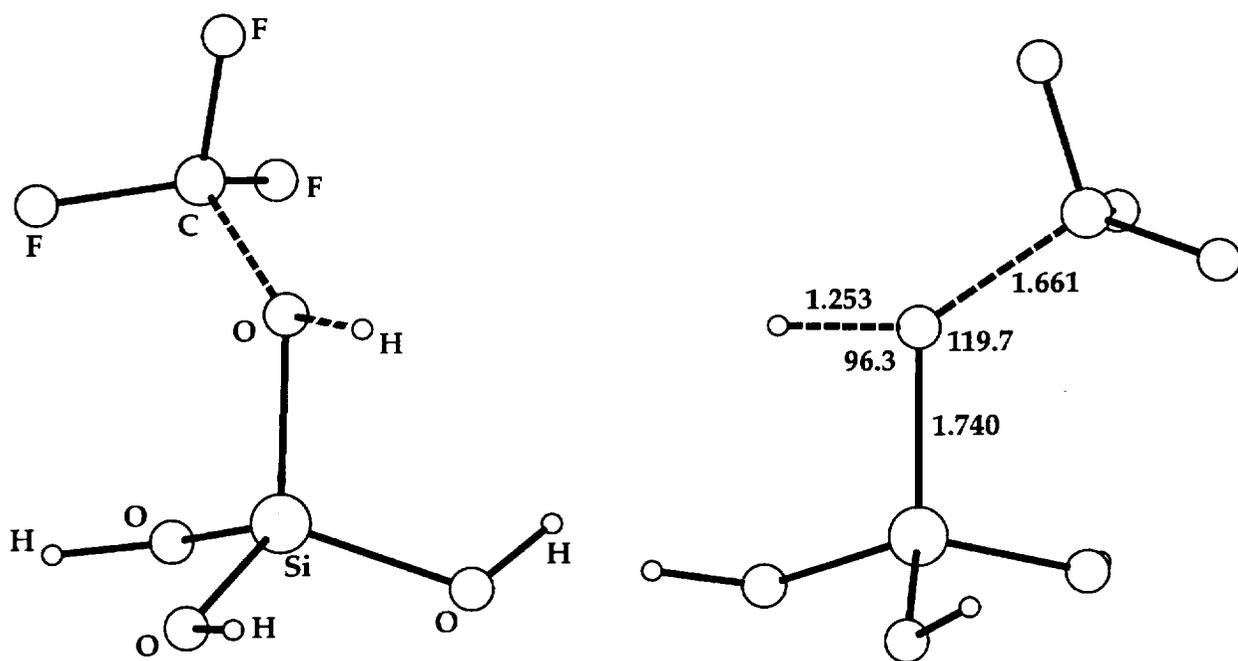


Fig 4